EFFICACY OF RESPIRATORY PROTECTIVE EQUIPMENTS AGAINST SOLID PARTICLES COMING FROM FRICTION PROCESSES IN TRAFFIC

ČABANOVÁ Kristina[1,2], SEIDLEROVÁ Jana[1], PEIKERTOVÁ Pavlína[1], RAJHELOVÁ Hana[1], MOTYKA Oldřich[1], VACULÍK Miroslav[1,2], KUKUTSCHOVÁ Jana[1,2]

[1]*VSB - Technical University of Ostrava, Nanotechnology Centre, Ostrava, Czech Republic, EU*

[2]*Regional Materials Science and Technology Centre, VSB - Technical University of Ostrava; Czech Republic, EU*

Abstract

Friction associated with wear, representing non-combustion processes in traffic can pose a problem for the human health, mainly in terms of exposure to solid particles. During braking, substantial amounts of micron and sub-micron metal based particles are released into the environment. The aim of this pilot study was to evaluate whether these particles could reach the human body via respiratory exposure even when respiratory protective equipment is used. In this study, workers were exposed to resuspended dust particles for one hour during automotive brake dynamometer maintenance (particle removal and machine cleaning). The particles deposited in the dynamometer were generated during the laboratory tests of the friction performance of brakes using different types of friction composites. Throughout the course of the work, workers wore respiratory protective equipment to prevent particulates from entering the respiratory tract. These protective devices are being used in accordance with EN 140:1998 guidelines for protection against fine dust, water and oil-based liquid aerosols, viruses, bacteria, spores, organic and acid gases, vapors and ozone. A sample of saliva for the detection of trapped particles was analysed using scanning electron microscopy and Raman microspectroscopy. Quantification of these captured particles was performed by inductively coupled plasma atomic emission spectrometer and inductively coupled plasma mass spectrometer. The results show that in the saliva of the workers, particles/agglomerates of metal particles in micron and submicron dimensions were present, with the majority of Al, Fe, Ba, Zn, Cu, Sn, and Bi, which were present in the saliva of the workers even after an hour from the exposure to the wear particles despite wearing respiratory protective equipment.

Keywords: Respiratory protective equipment, metal based particles, Raman microspectroscopy, scanning electron microscopy, atomic emission spectrometry

1. INTRODUCTION

Materials for automotive friction brake pads generally consist of four main groups of components: binders, reinforcing agents, fillers, and friction modifiers (lubricants and abrasives). The binders hold the other components together and make up 20-40% of the brake linings. They are mainly phenol-formaldehyde resins. Reinforcing agents, mainly fibers primarily provide mechanical strength of the brake and make up approximately 6-35% of brake lining mass. They can be metallic, mineral, ceramic or organic, (examples of materials: copper, steel, brass, titanium glass). Fillers, which represent about 15-70% of the brake linings, are used to improve the thermal properties of a brake. They consist of inorganic compounds (barium and antimony sulphate, magnesium and chromium oxides), as well as ground slags, silicates and metal powders. Lubricants are usually used to reduce the wear of the lining. They may be inorganic, metallic or organic. It forms about 5-29% of the weight of the brake lining. Most commonly graphite is used as a lubricant, but also ground rubber, metal particles, carbon black, dust, cashew nuts, clay minerals and antimony trisulfide. Abrasives are mainly used to increase friction between surface of pad and rotating disc. These include aluminum oxides, iron oxides, quartz and zirconium and make up about 10% of the lining weight [1-4]. The exact composition of individual commercial brake linings is not available, largely due to confidential character of this information. However, the individual components of the brake lining, when exposed to high temperatures and pressure, may be released into the environment in form of particles having chemistry and morphology significantly different from the inital material. Sizes of such released particles may be down to tens of nanometers [5,6]. The easiest and most common route of particle entry into the body is through inhalation exposure, i.e via respiratory system. Under normal conditions, the gas is exchanged between the blood and the external environment. To protect the respiratory tract from non-toxic, irritating and toxic dusts, various protective devices are recommended to be used in and outside the work environment. The easiest way is to use a respirator that is technically referred to as a filter mask. Filter masks / masks must meet the requirements of European Standard EN 140:1998 [7]. In terms of filtration efficiency, half masks are divided into three classes: P1 - non-toxic dust (cement, aluminum, magnesite, ash, abrasive powder, soil dust, soot, limestone, slag, marble, etc.), P2 - against dust with predominantly irritating effect (resins, PVS, fiberglass, wood, tobacco, etc.), P3 - against toxic particles, viruses, bacteria, spores and radioactive dust.

The aim of this pilot study was to evaluate whether particles, generated through non-combustion processes in transport, could reach the human body via respiratory exposure even though respiratory protective equipment.

2. MATERIAL AND METHODS

2.1. Studied samples

Workers were exposed to resuspended dust particles for one hour during brake dynamometer maintenance (particle removal and machine cleaning). The particles deposited in the dynamometer were generated during the laboratory tests of the friction performance (according to ISO standard 26867:2009) using different formulations of friction composites [8]. Throughout the course of the work, workers should wear respiratory protective equipment together with a pair of P3 filters. These protective equipment, which should prevent particulate matter from entering the respiratory tract, are being used in accordance with EN 140:1998 guidelines for protection against fine dust, water and oil-based liquid aerosols, viruses, bacteria, spores, organic and acid gases, vapors and ozone. Sample for identification of trapped particles were collected before and after the exposure to dust particles. Samples of saliva were then placed in formo f drops of 200 μl in volume on a glass slide in 10 layers, each layer was left to dry separately in an antiseptic flowbox Steril Bio Ban Compact (Schoeller). To prevent contamination, the samples were stored in the desiccator between the individual analyzes.

2.2. Methods used

Raman spectra were obtained using the Smart Raman microscopy system XploRATM (HORIBA JobinYvon, France) in the entire range of wavelengths from 100 to 4000 cm^{-1}. Lens with magnification 100x was used, because it is suitable for samples in the form of thin films. A laser of 532 nm (20 - 25 mW) was used. The laser spot diameter was approximately 0.5 µm, which allows for a particle / aggregate spot analysis. Intensity of the laser beam was reduced to 1, 10, or 25 % of its initial intensity to prevent damage of the samples. The grid was set to 1200 grooves / mm. This method is non-destructive, thus the sample can be used for further analysis.

For more detailed characterization of the morphology, size, and elemental composition of the detected solid particles, scanning electron microscopes XL30 (Philips) and the Quantum FEG 450 (FEI) equipped with the APOLLO X (EDAX) analyzer were used. Two detectors were used for the measurements: SE - secondary electron detector and BSE - backscattered electron detector. In addition, an X-ray detector for sample microanalysis (SEM - EDS) was used.Atomic emission spectroscopy with inductively coupled plasma (AES - ICP) was used for chemical analysis. The AES-ICP spectrometer (SPECTRO Ciros Vision EOP, Germany) is equipped with an Ar/Ar plasma torch unit (argon, purity 4.6 was used), a flow nebulizer and a CCD detector.

3. RESULTS AND DISCUSSION

The elements detected in all saliva samples by AES-ICP are listed in **Table 1**.

Table 1 Overview of AES-ICP results of saliva samples from dust exposed workers during dynamometer maintenance. A - before work, B - after work.

µg/sample sample	Al	Ba	Co	Cr	Cu	Fe	Mn	Ni	Zn
1A	>0.75	0.15	>0.075	>0.050	>0.15	2.49	0.24	>0.075	0.17
1B	**0.93**	**0.87**	**0.078**	**>0.050**	**0.48**	**15.2**	**0.63**	**0.11**	**0.42**
2A	>0.75	0.16	>0.075	>0.050	>0.15	0.30	0.034	>0.075	0.066
2B	**0.75**	**0.31**	**>0.075**	**>0.050**	**0.17**	**3.18**	**0.49**	**0.094**	**0.45**
3A	>0.75	0.17	>0.075	>0.050	>0.15	0.34	0.062	>0.075	0.23
3B	**2.22**	**2.07**	**0.58**	**0.45**	**1.03**	**105**	**1.33**	**0.11**	**3.85**
4A	>0.75	0.16	>0.075	>0.050	0.22	2.33	0.33	>0.075	0.70
4B	**>0.75**	**0.28**	**0.077**	**>0.050**	**0.40**	**10.6**	**0.36**	**>0.075**	**0.88**

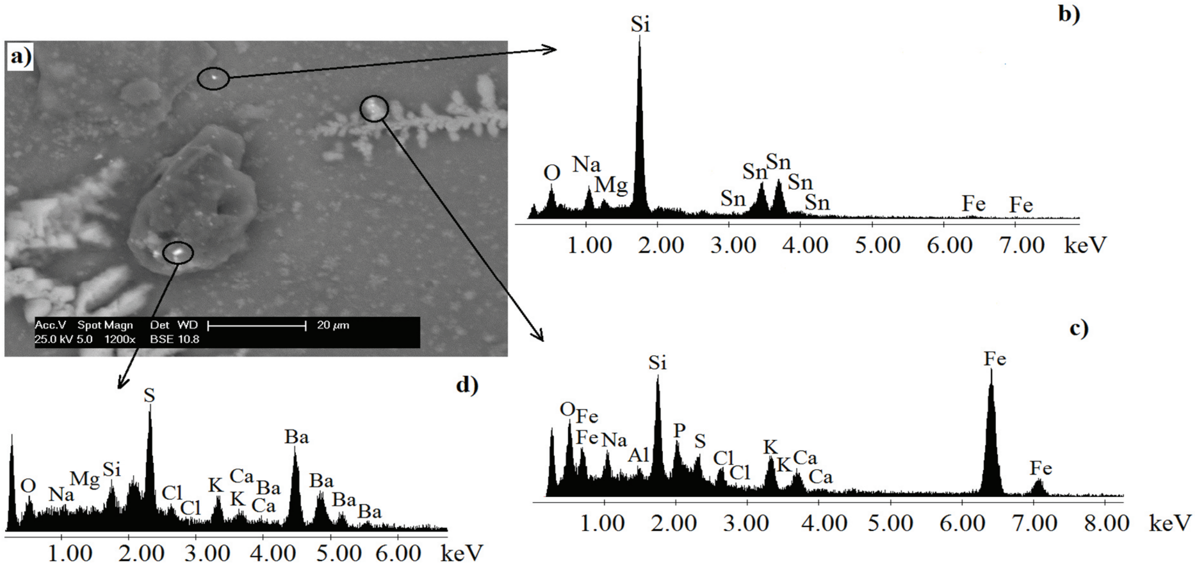

Figure 1 Particle mainly based on tin b), particle mainly based on iron c), and particle mainly based on barium d), detected by SEM - EDS. These particles were found in a sample of saliva after the exposure a)

The P3 - Particulate and Ozone Active Filters, which comply with EN 148:1998, have their limits of effectiveness as 50x the permissible exposure limit (PEL). "The permissible exposure limit (PEL) of a chemical or dust is the time-weighted average gas, vapor, or aerosol concentration in the working atmosphere, to which an employee may be exposed to an eight-hour or shorter shift of weekly working hours according to the current state of knowledge, lifetime occupational exposure to health damage, endangering his / her working ability and performance" [9]. However, there is no information provided on the smallest particle sizes for which the filters with P3 efficiency are efficient. Through SEM - EDS, particles with the majority content of Al, Ba, Bi, Cu, Fe, Ti, Sn and Zn were detected in saliva taken after exposure. The selected spectra are shown in **Figure 1** and **Figure 2**. The particle/cluster sizes ranged from 2 to 5 µm.

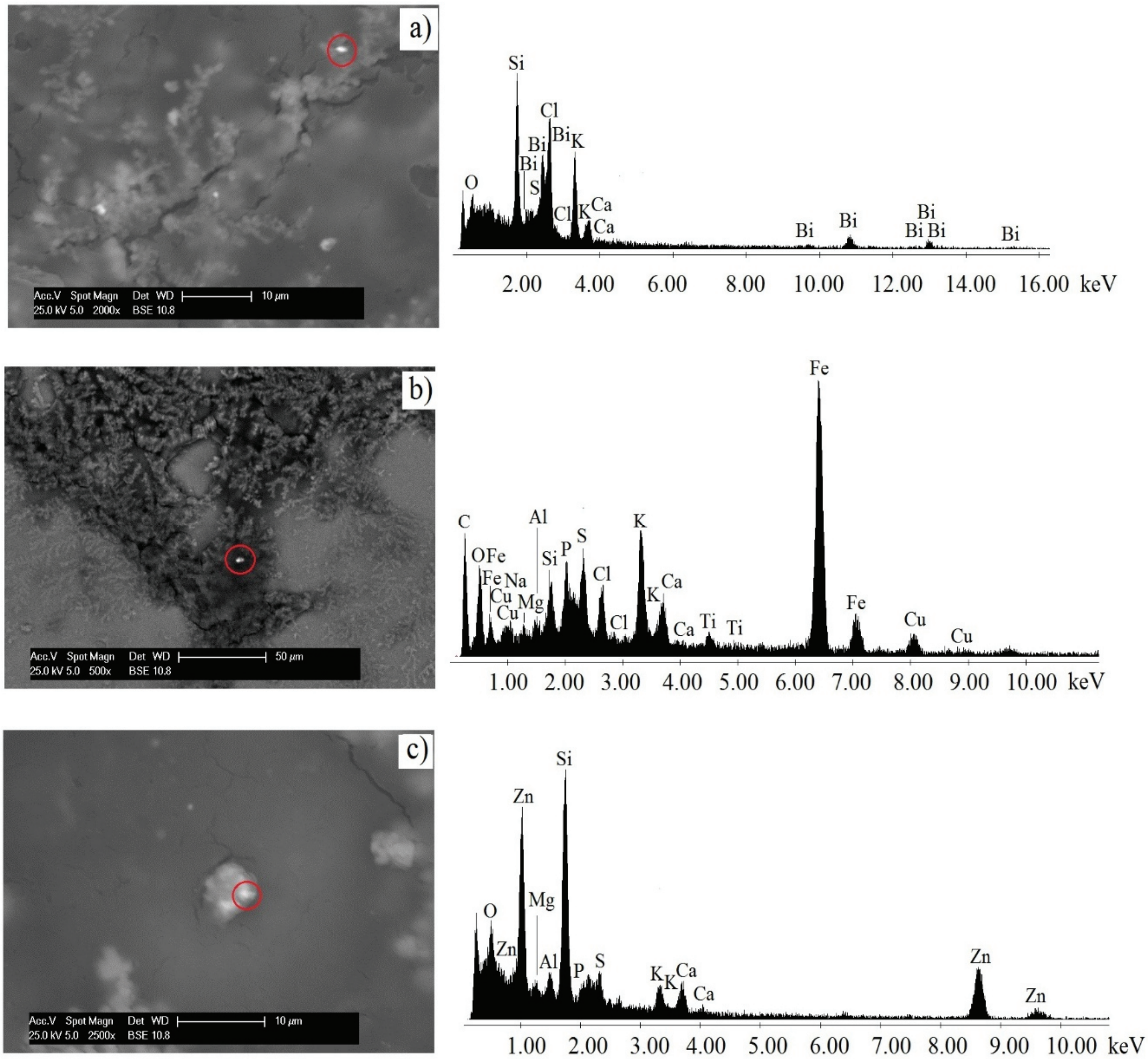

Figure 2 Particle mainly based on bismuth a), particle mainly based on copper and iron b), and particle mainly based on zinc c), detected by SEM - EDS. These particles were found in a sample of saliva after the exposure.

It is already known that braking of automobiles generates also nanoparticulate emissions with sizes down to 20 nm and the majority of these particles are mainly carbon black and metal oxides, as well as other metallic compounds [1,10]. At the same time, automotive braking also produces tire and road surfaces abrasions, where particles can be in sizes down to 6 nm. These particles are complex of substances, mainly zinc compounds, organic polymers, but also metals such as Li, Na, Ca, Fe and Ti [6,10]. Specifically, non-combustion processes in the transport (wear of brakes) are also a source of baryte ($BaSO_4$). During the braking process, brake pads are worn, and some of the brake components can be released into the environment [11]

From **Table 1** it is evident that the number of all detected elements was clearly higher for workers after dynamometer maintenance. These were mainly Al, Ba, Fe, Cu, Mn and Zn based particles. Titanium in saliva samples after the exposure was not found. However, one of the phases of titanium dioxide - rutile and also amorphous carbon was detected using Raman microspectrometry - sample 3B (**Figure 3**). According to International Agency for Research of Cancer (IARC), these samples based on their composition may be classified as an agent "prominently carcinogenic to humans". These hazardous components are mainly Cr^{IV}, Fe (not differentiated form), Ni (compounds) and soot. The group of "possible carcinogens for humans" includes detected particles of Ni (metal, alloy), and TiO_2 [12].

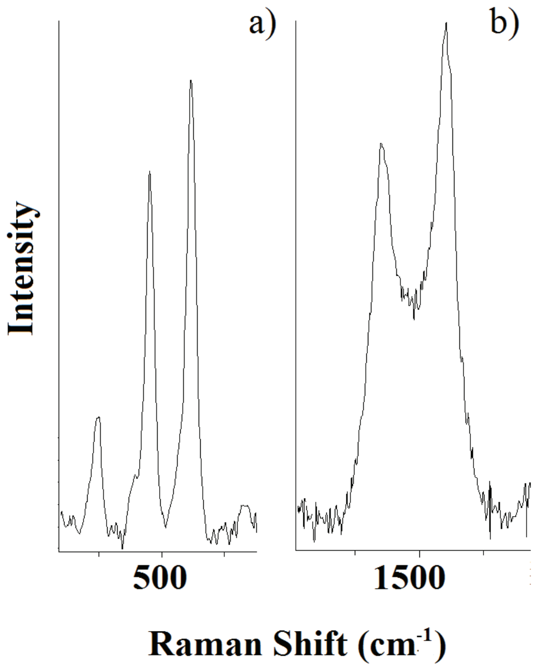

Figure 3 Spectra obtained using Raman microspectrometer. Spectrum a) TiO_2 as rutile phase and b) amorphous carbon were identified

The effectiveness of the respiratory protective half-mask used together with the P3 filters was not sufficient and largely did not capture the resuspended dust generated during the laboratory friction performance tests using different formulations of friction composites. In some studies, it has also been found that the effectiveness of tested respiratory masks is considerably worse than that required by the European standards. According to the authors, this could be due to a high concentration of dust used in testing (800 mg / m^3) or a poorly sealed mask [13].

4. CONCLUSION

All elements detected using AES - ICP were in higher concentrations for workers after the performed work. The detected particles were based mainly on Al, Ba, Fe, Cu, Mn and Zn. SEM - EDS revealed particles with the major content of Al, Ba, Bi, Cu, Fe, Ti, Sn and Zn in saliva taken after the exposure. An amorphous carbon and rutile phase of the titanium dioxide were detected by Raman microspectroscopic analysis. Some of the substances detected in saliva after the exposure include its chemical composition according to IARC, an agent "probably carcinogenic to humans or belonging to the group" possible carcinogens for humans". The effectiveness of the respiratory protective half-mask used together with the P3 filters was not sufficient and did not capture entirely the dust generated during the laboratory friction performance tests.

ACKNOWLEDGEMENTS

This paper was created on the Faculty of Metallurgy and Materials Engineering in the Project No. LO1203 "Regional Materials Science and Technology Centre - Feasibility Program" funded by Ministry of Education, Youth and Sports of the Czech Republic, and supported by project reg. no. SP2016/78, and SP2017/75 (Ministry of Education, Youth, and Sports of the Czech Republic).

REFERENCES

[1] KUKUTSCHOVÁ, J., MORAVEC, P., TOMÁŠEK, V., et al. On airborne nano/micro-sized wear particles released from low-metallic automotive brakes. *Environmental Pollution*, 2011, vol. 159, no. 4, pp. 998-1006.

[2] GRIGORATOS, T., MARTINI, G. Brake wear particle emissions: a review. *Environmental Science and Pollution Research*, 2014, vol.22, pp. 2491-2504.

[3] CHAN, D., STACHOWIAK, G.W. Review of automotive brake friction materials. *Proceedings of the Institution of Mechanical Engineers, Part D: Journal of Automobile Engineering*, 2004, vol 218, pp. 953-966.

[4] THORPE, A., HARRISON, R.M. Sources and properties of non-exhaust particulate matter from road traffic: a review. *Science of the Total Environment*, 2008, vol. 400, pp. 270-282.

[5] KUKUTSCHOVÁ, J., ROUBÍČEK, V., MALACHOVÁ, K., et al. Wear mechanism in automotive brake materials, wear debris and its potential environmental impact. *Wear*, 2009, ol 267, no. 5-8, pp. 807-817.

[6] DALL´OSTO M., BEDDOWS, D., GIETL, J., et al. Characteristics of tyre dust in polluted air: Studies by single particle mass spectrometry (ATOFMS). *Atmospheric Environment*, 2014, vol. 94, pp. 224-230.

[7] ČSN EN 140/1998, Czech Technical Standard. Respiratory protective devices - Halfmasks and quarter masks - Requirements, testing, marking.

[8] ISO 26867:2009. Road vehicles -- Brake lining friction materials -- Friction behaviour assessment for automotive brake systems.

[9] ŠAMÁNEK, J., BAUMRUK, J. Přípustné expoziční limity chemických látek v pracovním prostředí. *SZÚ - Centrum odborných činností v OPVZ. 2010. dostupné z:* http://www.szu.cz/tema/pracovni-prostredi/pripustne-expozicni-limity-chemickych-latek-v-pracovnim-prostredi.

[10] FILIPOVÁ, Z., KUKUTSCHOVÁ, J., MAŠLÁŇ, M. *Rizika nanomateriálů* 1st ed.Olomouc: Palacky University in Olomouc, 2012, 88 p.

[11] KUKUTSCHOVÁ, J., ROUBÍČEK, V., MAŠLÁŇ, M., et al. Wear performance and wear debris of semimetallic automotive brake materials. *Wear.*2010, vol.268, no. 1-2, pp. 86-93:

[12] Agents Classified by the IARC Monography. International Agency for Research on Cancer [online]. Lyon, France: Lyon CEDEX 08, 2017 [cit. 2017-08-31]. Dostupné z: http://monographs.iarc.fr/ENG/Classification/

[13] GRIMA-OLMEDO, C., RAMÍRÉZ-GOMÉZ, Á., MEDIC-PEJIC, L., et al. The penetration of respiratory protective devices by respirable solid particles. *Journal od Aerosol Science.2014, vol.74, pp. 36-41.*